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Chapter 6

Crystals in Materials Science

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Additional information is available at the end of the chapter

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1. Introduction

Intense and sustained research into single crystals and polycrystalline assemblies continues to produce advanced materials crucial to the function of modern and future electronic and photonic devices. Device function is not only based upon the optical and electronic properties of the active material (for example, the light absorbing layer in molecular solar cells), but also the molecular and supramolecular ordering. Herein we will focus on devices and technologies where single crystalline materials are employed, and where appropriate, discuss competing materials and devices where polycrystalline or amorphous materials are used. We acknowledge that there is a sustained push to use solution processable conjugated polymer films for several similar technological applications; however, these films are typically disordered and suffer from impurities and chemical defects inherent to synthetic macromolecules making definitive characterization using X-ray diffraction difficult or impossible. Small molecule crystalline materials, on the other hand, can be obtained in high purity with a high level of organization in the solid state.

Additionally, our discussion will be largely limited to organic materials as there is a drive to replace conventional inorganic active materials (for example the semiconductor channel layers in transistors) with organic compounds. The reasoning for this lies in the fact that organic compounds can be synthesized and purified relatively easily using bench-top techniques without the requirement of high temperatures and energy intensive processes. As an example, to obtain electronics and solar cell grade silicon several high temperature steps are required to reach the necessary purities in excess of 99.9999%.[1] Organic compounds can be highly purified using conventional solution crystallization or vapor growth[2] methods yielding materials which exhibit impressive performance, in some cases rivaling their inorganic counterparts.[3]

For this review we selected to focus on two areas: (i) photochromic molecules that can be used for molecular scale data storage and as actuators capable of turning molecular level changes into macroscopic motion, (ii) organic field effect transistors and organic photovoltaics that

make use of single crystals for charge transport. Other important areas of research such as catalysis, nonlinear optics, magnetic materials, and biology also make effective use of crystalline materials but are beyond the scope of this review.

2. Photochromic materials

Photochromism is the light induced reversible change in the absorption spectrum of a molecule and is necessarily accompanied by changes in both electronic and molecular structure and properties.[4] A generic photochromic system in which component A can be transformed into B via irradiation with light of energy $h\nu_1$ is illustrated in Figure 1. Species B reverts back to A upon exposure to light with energy $h\nu_2$. As photochromic molecules have the ability to optically cycle between two spectroscopically distinct states, they have been studied for possible applications in molecular switching, variable transmission lenses, and molecular scale optical data storage.[5] In some cases a system may also have a thermally activated pathway for the interconversion of the chemical species. Given the close packing and perceived rigidity of crystalline lattices, photochromism in the crystalline state was thought to be rare compared to observation of this phenomenon in solution[6] or in polymer matrices[7] where the medium is less constrained and thus permits the associated changes in molecular shape and volume.

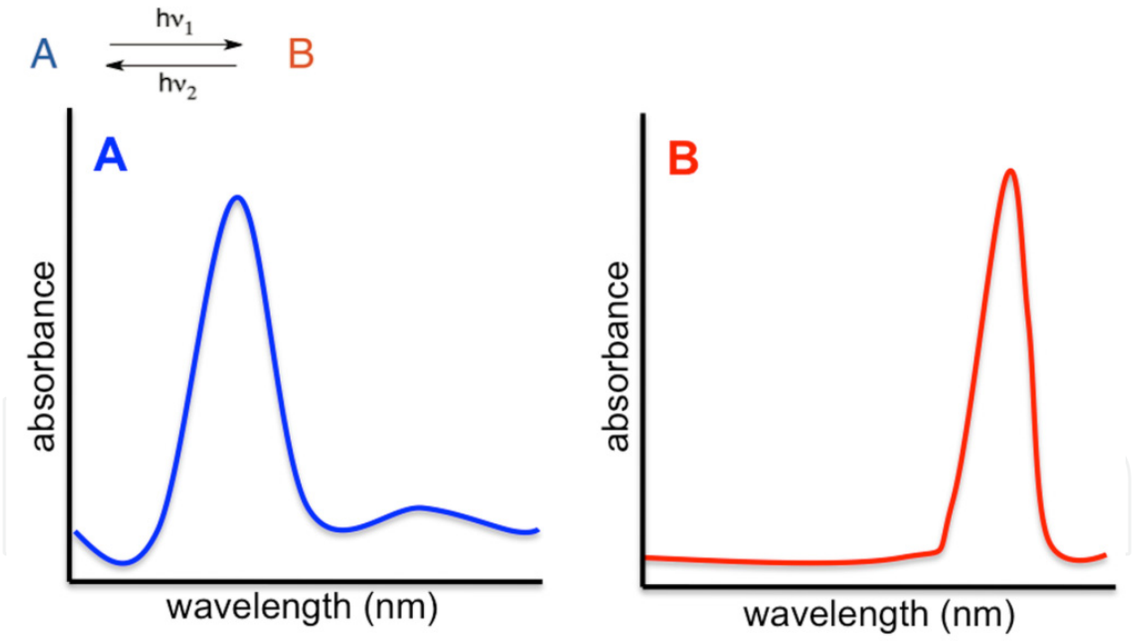
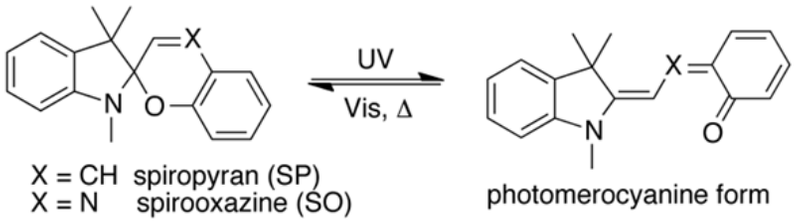


Figure 1. Photochromic compounds can interconvert by irradiation with light of different wavelengths. The two components, A and B, of a system have different absorption spectra. Though not specifically shown, a thermal pathway to interconversion may be present.

The spirooxazine (SO) and spiropyran (SP) class of photochromic materials are typified by a heterocyclic ring-closed isomer, the spiro-form, which is usually colorless and dominates the equilibrium. The isomerization of representative SO and SP compounds is shown in Scheme 1. Irradiation with high-energy UV light leads to cleavage of the C-O bond at the spirocyclic

carbon giving a ring-opened form, the photomerocyanine form, that is strongly colored owing to the extended conjugation afforded by planarity and the donor-acceptor character of the molecule.[5, 8] Removal of the UV irradiation source or irradiation with visible light affects the reverse reaction. While photochromic spiropyrans[9] and spirooxazines[10] have been known for some time, photoisomerization has almost exclusively been observed in solution and in polymer matrices, though recent research suggests that crystalline state photoisomerization may be more general and thus make SOs and SPs amenable to use in solid state devices. Understanding and visualizing the structural and electronic changes that occur upon photoisomerization would be indispensable in aiding the design and fabrication of SO and SP containing devices and guide the synthesis of new materials.



Scheme 1. General structure of spirooxazines and spiropyrans. Photoisomerization is initiated with UV light; visible light or heat affects the ring closing reaction.

More than ten years ago, Benard and Yu used UV-Vis absorption measurements to show that photoisomerization occurred in microcrystalline powders of cationic SO **1**[11] and SPs **2** and **3**[12] shown in Figure 2. This was attributed to the presence of a large iodide counter ion giving the necessary free space in the crystal lattice along with stabilization of the iminium cation that was afforded upon ring opening. When examined by X-ray diffraction, however, the powder patterns showed only small changes suggesting that the observed isomerization was likely a surface effect and did not occur in the bulk.

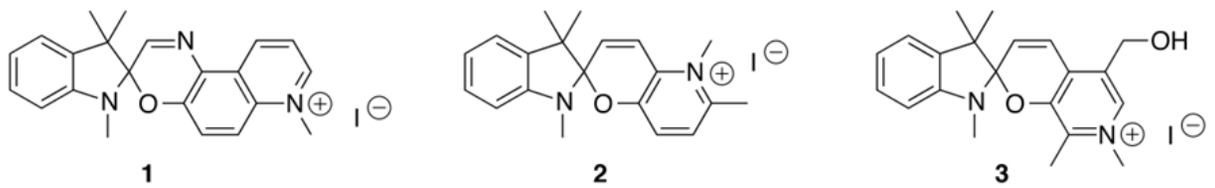


Figure 2. Molecular structures of cationic spirooxazines and spiropyrans that show photochromism in microcrystalline powders.

Arguably, the single crystalline phase is more constrained than microcrystalline powders giving less room for the large structural changes that are necessary upon ring opening and planarization in SOs and SPs. When the indoline group typically used for spirooxazines is replaced with an azahomoadamantyl group as in SO **4** (Figure 3), isomerization was found to occur at room temperature in prism shaped single crystals grown from a hexanes solution.[13] The initially colorless, block shaped crystals turned dark purple upon irradiation with UV light. Unlike in solution, the thermal reaction leading to color bleaching was not observed in the single crystal, and the dark purple color persisted for several months compared to seconds or minutes in solution. Analysis of the electron density difference map

(Figure 3c) showed only small changes indicating that there was likely much less than 10% photoconversion within the crystal.[14] The polarized absorption spectra before and after irradiation (Figure 3d) illustrate the dramatic changes in the absorption spectra that occur upon photoisomerization. These results demonstrate that crystalline SO materials could be used as filter materials and possibly as data storage media where the differences in absorption could correspond to the 1's and 0's of the binary computer language. It should be noted that changes in the polarizer orientation do not lead to significant changes in absorption because of the orthogonal arrangement of molecules in the crystal lattice.[13] The exact structure of species responsible for the purple color was never discussed, although it may be some ring opened form that is not completely planar through the conjugated portion and that may not be able to revert to the closed form owing to crystal packing forces.

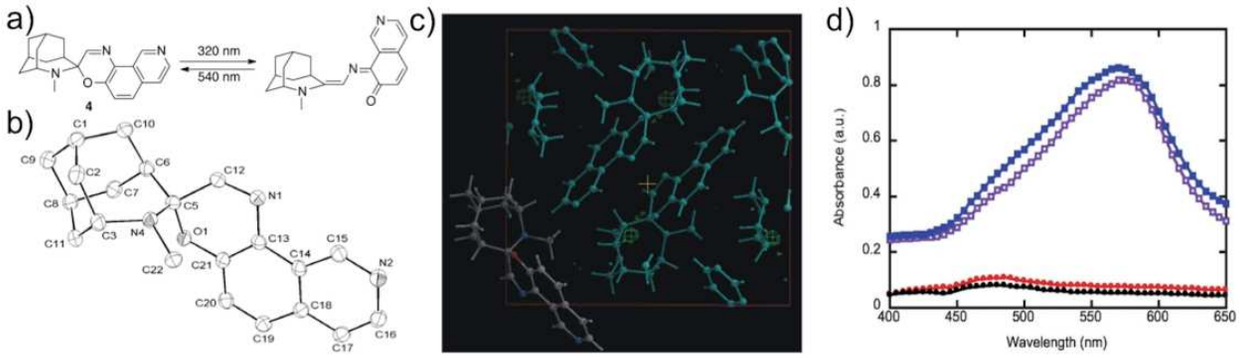


Figure 3. (a) Molecular structure and photoisomerization of SO **4**, (b) crystal structure of SO **4**, (c) the electron density difference map of a single crystal of **4** before and after irradiation with UV light, and (c) polarized absorption spectra of **4** before UV irradiation with the polarizer at 0° (red circles) and 90° (black circles), and after irradiation with the polarizer at 0° (purple squares) and 90° (blue squares) relative to the [011] plane. The electron density difference map is defined as the difference between the electron density map of an irradiated single crystal and that of the same crystal before irradiation. Thermal ellipsoids are shown at the 50% probability level with hydrogens omitted for clarity. (Figure adapted from reference 13. Reproduced by permission of The Royal Society of Chemistry).

Harada and coworkers[15] reported similar results for the irradiation of single crystals, obtained from methanol or acetone solution, of a series of structurally related SOs and SPs at various temperatures. UV irradiation at room temperature resulted in little or no color changes. In contrast, irradiation of the single crystals at 90 K led to strong color changes that persisted. The population of the photogenerated form was low, however, as it could not be detected by X-ray diffraction. The supposition was made that the thermal reversion to the colorless spirocyclic form is fast at room temperature and thus cryogenic temperatures essentially prevent this reaction. The authors note that it is unclear whether these single crystal photoreactions occur at defect sites or whether lattice control is directly responsible and investigations to answer this question are currently underway.

In contrast to the spirooxazine and spiropyran class of photochromic materials, diarylethenes require only modest structural changes upon photoisomerization. The observed isomerization is typically not thermally reversible if aryl groups with low aromatic stabilization energy such as thiophene, benzothiophene, furan, and thiazole are used.[18]

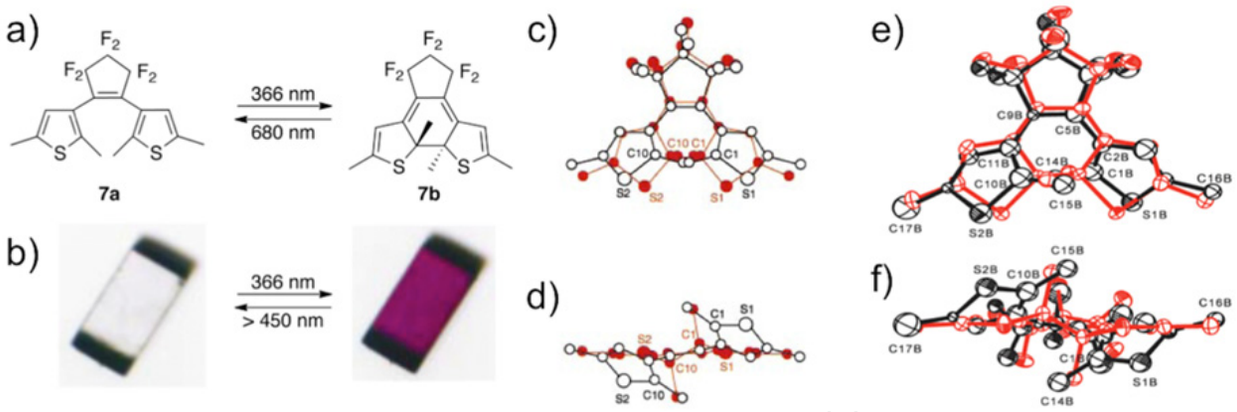


Figure 4. (a) Molecular structure of dithienylethene **7** that is photochromic in the single crystal. (b) Photograph of a single crystal of **7a** under polarized light before (left) and after (right) UV irradiation. (c) Top view and (b) side view of the movement of each atom of **7a** in the crystal during photoisomerization and relative atom positions of **7a** (O, open circles) and **7b** (b, red circles). (e) Top view and (f) side view of the molecular structure of a crystal of **1b** before and after irradiation with 680 nm light for 100 h: The closed-ring form **1b** and open-ring form **1a** resulting from irradiation were drawn by red and black lines, respectively. The ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. (Adapted with permission from references 16 and 17. Copyright 1999 and 2000 American Chemical Society).

Initial work by Irie and Uchida[18] showed that a single crystal of a thiophene substituted perfluorinated diarylethene exhibited the photoisomerization phenomenon in the single crystalline phase. A single crystal of this compound, which was initially clear and colorless, became reddish upon irradiation with UV light. As a proof of concept that these crystals could be used for data storage, the authors inscribed the Chinese character for "light" on the crystal with micron dimensions.[18]

Subsequent work has shown that photoisomerization in diarylethene single crystals is a rather general phenomenon.[16-17, 19] The compound 1,2-bis(2,5-dimethyl-3-thienyl) perfluorocyclopentene (compound **7**), shown in Figure 4 in its ring opened (**7a**) and ring closed (**7b**) forms, serves as a quintessential example.[16] Single crystals of **7a** grown from hexanes are rhomboid in shape and colorless. Irradiation with 366 nm light causes the crystal to turn reddish purple in color (Figure 4). Polarized absorption spectra showed that the changes in absorption occurred without loss of order in the crystal and X-ray diffraction experiments confirmed that ring closed isomer **7b** was formed. Figures 4c and 4d show an overlay of the molecular structure of **7a** and **7b** and it can be clearly seen that the majority of motion occurs in the region of the sulfur and reacting carbon atoms (atoms C1 and C10). To show that the ring opening reaction was also possible, crystals of **7b** were also grown and irradiated with visible light.[17] The conversion (**7b** to **7a**) was only about 9% but did prove that this reverse transformation was also possible. When an organometallic diarylethene **8** (Figure 5) was synthesized, it exhibited even higher photoconversion factors in the single crystalline phase. The isomerization was found to proceed through a triplet sensitized pathway leading the authors to conclude that crystals of such compounds could easily find use as molecular switches.[20]

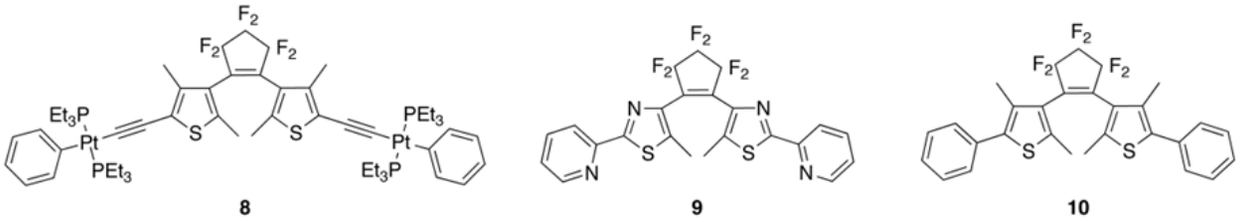


Figure 5. Molecular structures of ring open diarylethenes that photoisomerize to the ring closed form in the single crystalline state. Compounds **9** and **10** demonstrate additional photomechanical properties.

The ability to efficiently photoisomerize in the single crystalline phase endows diarylethenes with the unique ability to use light to carry out a change on the molecular level that then leads to action on the macroscopic scale. Colombier and coworkers observed irradiated diarylethene crystals of **9** (Figure 5) "jump" distances of 500 μm; when crystals are immobilized and unable to "jump" cracks appear on the surface.[21] While the jumping phenomeon was not observed in compound **10** (Figure 5), these crystals showed reversible surface morphology changes as determined by atomic force microscopy (AFM) when alternately irradiated with UV and visible wavelength light. This observation led Irie and coworkers to examine the possibility of using suitably sized diarylethene crystals as actuators to perform mechanical work using light activation.[22]

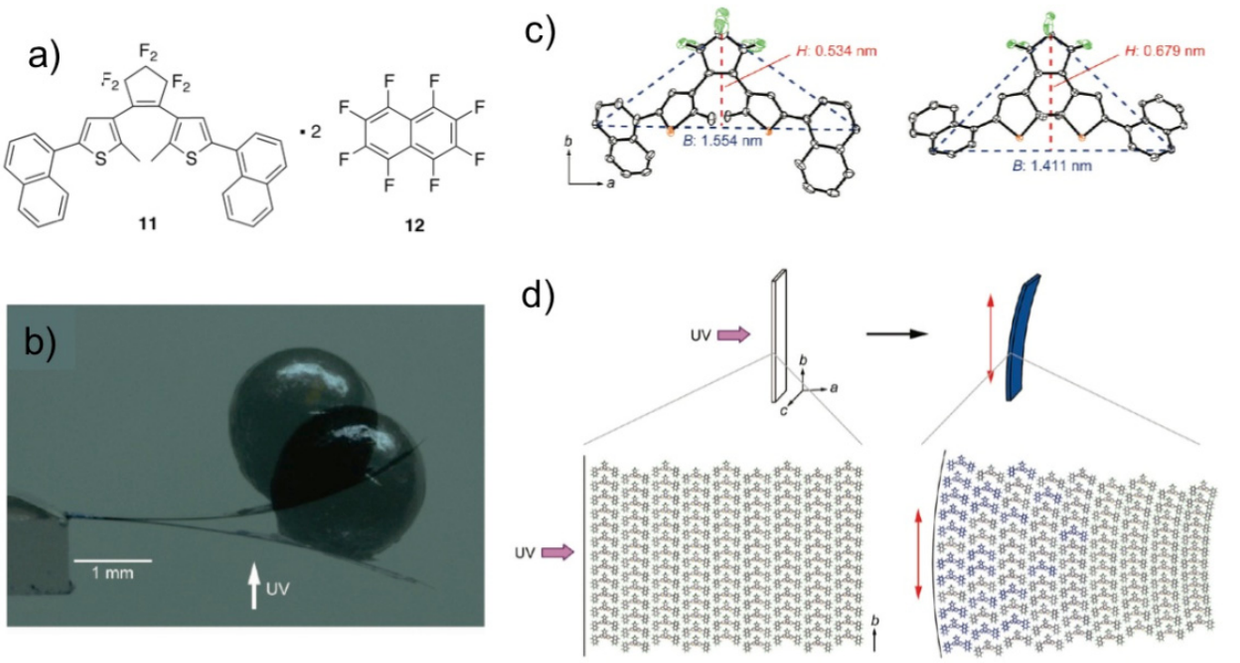


Figure 6. (a) Diarylethene **11** and perfluoronaphthalene (**12**) components of a co-crystal capable of photomechanical work. (b) Image of a rod-like co-crystal of **11** and **12** lifting a 2mm diameter, 46.77 mg lead ball after the application of UV light. (c) ORTEP diagram of **11** in the ring-opened and ring-closed forms with dimensions given for the long and short axis of the molecule. (d) Crystal packing in the co-crystal of **11** and **12** showing how photoisomerization at the molecular level leads to deformation in the crystal. The blue molecules are the ring-closed forms obtained after UV irradiation. (Adapted with permission from reference 23. Copyright 2010 American Chemical Society).

Initial attempts using single component rod-like crystals[22] or co-crystals consisting of a 1:2 molar ratio of diarylethene **11** and perfluonaphthalene (**12**)[23] demonstrated that photomechanical work was possible as the crystals were able to move a small load upon irradiation (Figure 6). When a rod-like crystal holding a small lead bearing was irradiated with UV light, the crystal bent away from the light source lifting the attached weight in the process. This effect is attributed to the change in the length of the short axis of the molecule (Figure 6c); when the molecules on the surface of the crystal are irradiated and photoisomerize to their ring closed state the net effect is an expansion on one side of the crystal (Figure 6d) which manifests as the macro-scale bending observed. The co-crystals proved quite durable by withstanding a few hundred cycles without degrading compared to less than one hundred cycles for the single component crystals.

Recent literature reports indicate that macroscopic motion due to molecular scale photoisomerization reactions is not unique to the diarylethene class of photochromes. A dimethylamino-subsistuted azobenzene, compound **13** in Figure 7, was shown to exhibit crystal bending despite the fact that a large change in molecular geometry is required upon photoisomerization, namely a *trans* → *cis* rearrangement.[24] Another compound worth mentioning is salicylideneaniline **14**, which has been known to undergo tautomerization in single crystals.[14] Small plate-like microcrystals (73 x 4.5 x 1.1 μm) were grown by sublimation, and when irradiated with 365 nm light bent in a direction away from the light source.[25] Irradiation with visible light returned the crystals to their former position. X-ray diffraction experiments confirmed that approximately 10% of the molecules had photoisomerized. Thus, it has been hypothesized that photochromic actuators could find use in artificial muscles and devices where light initiated photoisomerization is effectively translated into macroscopic motion.

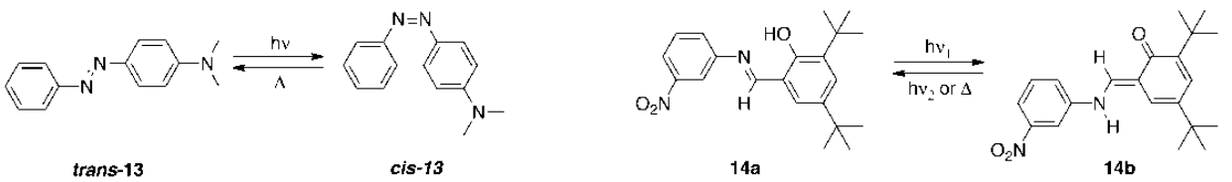


Figure 7. The molecular structures of photochromic azobenzene **13** and salicylideneaniline **14**. Both compounds show photomechanical effects in the single crystalline state.

In addition to mechanical and optical effects, the change in bonding pattern associated with the photoisomerization process has been explored as related to its influence on magnetic properties. In particular, the differences in conjugation between the two components of a photochromic system containing magnetic centers can lead to switchability in magnetic properties. Magnetism arises from the motion of charge, in particular unpaired electrons. Therefore, metal ions or organic radicals are typically employed and the resulting magnetic properties explored using single crystalline or microcrystalline materials.

Using the highly versatile diarylethene molecular framework, Irie showed that coupling between two terminal nitronyl nitroxide radical groups depended on whether the diarylethene was in its ring opened or ring closed form.[26] Microcrystalline powders of the

ring opened form showed little coupling between the two nitronyl nitroxide radicals, while the ring closed form showed strong anti-ferromagnetic coupling. This was attributed to the ability of the radicals to delocalize over the π-system, which was in turn dependent on whether the molecule was in its ring opened or ring closed state.

A relatively new means of controlling the magnetic properties of a material relies on the interaction between a metal center with unpaired electrons and a photoisomerizable ligand.[27] The ligand field, which in turn affects the magnetic behavior of the metal electrons, is predicted to change upon isomerization from one photochromic state to another. This has been clearly demonstrated by Nishihara[28] and one example illustrated in Figure 8. Irradiation of a microcrystalline styrylpyridine iron(II) based complex led to an increase in magnetization (measured on the y-axis) for a given temperature with the associated *Z* → *E* isomerization. X-ray crystallographic analysis of the isomers confirmed the observation of a change in magnetization.

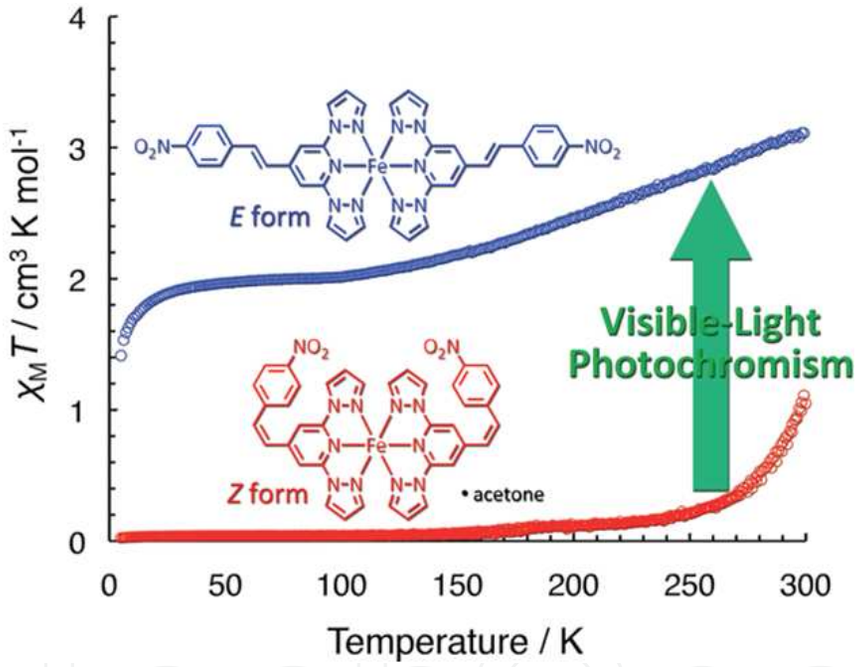


Figure 8. Photoisomerization of a styrylpyridine ligand leads to changes in magnetization of an iron complex at room temperature. (Adapted from reference 28. Copyright 2012 American Chemical Society).

3. Crystalline molecular semiconductors

No class of materials has been more important to the evolution of modern electronic devices than semiconductors. Inventions including the transistor, photovoltaics, and light emitting diodes all rely upon the semi-conductors unique ability to convert from electronically insulating to a fully conductive material. These devices typically require inorganic active materials that must undergo extensive and expensive processing to give materials of the required purity. Recently, there has been a push to replace traditional inorganic components with organic materials in the form of organic field effect transistors (OFETs) and organic photovoltaic (OPV) devices. While the subject of OPV and OFET fabrication and operation is

beyond the scope of this review, it is worth mentioning that one of the most important properties of a semiconducting material is its ability to conduct charge (referred to as the mobility and given in units of $cm^2/V•s$), either electrons or holes, and this is highly dependent on electronic structure, energy level (HOMO/LUMO) position, and on supramolecular organization.[29] Both π-conjugated polymers and small molecule based compounds have been examined, but only the molecular materials can be obtained in the required purity with the required supramolecular order that gives rise to the necessary charge transport properties.[30] The acene class of molecules shown in Figure 9 are among the most widely studied and best performing materials with regard to charge conductivity.[31]

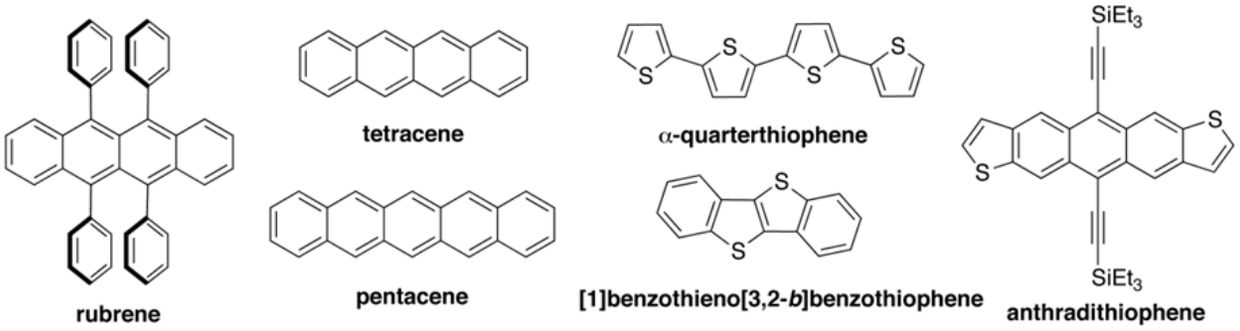


Figure 9. The structure of commonly used acene small molecules.

Facile processing is one of the greatest advantages organic materials hold over their inorganic counterparts. Organic molecules can be deposited on substrates in a number of ways including spin coating from solution, dip coating, vapor deposition methods, and ink-jet printing. The best performing materials are grown using the vapor deposition method,[2b] illustrated in Figure 10a, which can afford high quality single crystals while removing unwanted contaminants.[2a, 32] The single crystals are then manually harvested and manipulated into the appropriate device architecture. In contrast, dip-coating and other solution processing methods typically give lower quality materials relative to vapor-grown crystals (Figure 10b).

Although pentacene (structure show in Figure 9) was a popular molecule for OFET studies, rubrene (Figure 9) is now growing in popularity due to its superior stability in air as pentacene is easily oxidized.[34] Rubrene is known to exhibit several polymorphs depending on crystal growth conditions with packing also determined by competition between quadrupolar and π-stacking interactions.[35] It has the ability to form high quality crystals with an electronic band structure[36] as opposed to discrete energy states and was first examined as a single crystal OFET by Podzorov and coworkers who fabricated devices with mobilities as high as 1 $cm^2/V•s$[37] and up to 20 $cm^2/V•s$ with an optimized device.[38] Soon after, Brédas and coworkers compared the crystalline state structures of rubrene to unsubstituted acenes both computationally and experimentally and found that, contrary to expectation, the bulky phenyl side groups force molecular displacements that promote large intermolecular electronic coupling.[39] Furthermore, mobility was shown to be axially dependent.[40] However, when an "in channel" device was fabricated, where charge carriers moved through the bulk of the crystal as opposed to near the surface, mobility values of ~40 $cm^2/V•s$ were obtained

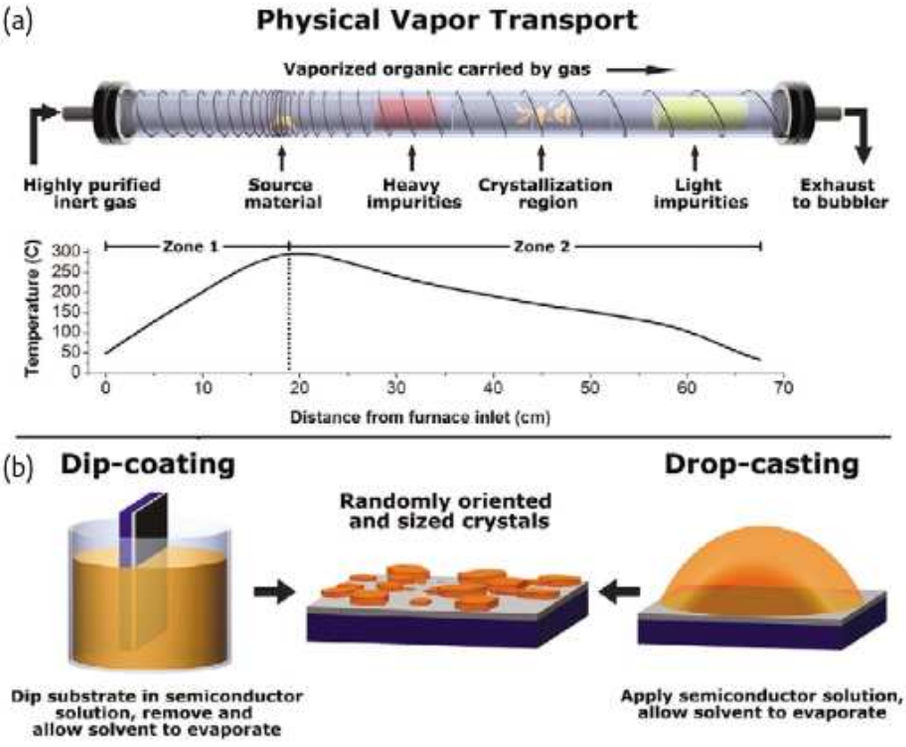


Figure 10. A schematic showing (a) the physical vapor transport method of single crystal growth contrasted with the (b) growth of crystals by solution methods. The physical vapor transport method offers crystals of high purity and greater uniformity. (Figure taken from reference 33 with permission).

thus showing that surface traps and adsorbed impurities greatly impact OFET performance. More importantly, the high mobilities measured in these materials indicate that organic single crystals are suitable for use in electronic devices.

Andrienko and coworkers[41] have suggested, that single crystal based OFETS may not be practical, likely owing to the delicate manipulations needed to make the devices coupled with the fragile nature of the crystals. Anthony and coworkers[31a, b, 42] have tried to synthesize acenes with solubilizing groups that can be deposited using solution methods while maintaining a high level of crystalline order. Examples of these soluble acenes are shown in Figure 11. Some of the derivatives show good mobilities (on the order of 1.0 $cm^2/V•s$) for solution-processed materials. Interestingly, small changes in the solubilizing groups lead to pronounced changes in the crystal packing as determined by X-ray diffraction. A triethylsilyl substituted acene (compound **16**) exhibited a brick-work[31c] packing motif that is ideal for maximized π-orbital overlap between neighboring molecules which translated into mobilities of 1.0 $cm^2/V•s$. A simple switch from the triethyl to the trimethylsilyl substituted acene (compound **17**) resulted in crystal structure that exhibited herringbone packing, negligible intermolecular orbital overlap, and mobilities that were too low to be measured.

Given the interest in making high quality single crystals or crystalline films of organic semiconductors for OFETs, new methods have emerged for the deposition of such structures. Inkjet printing techniques[43] have been shown to give microcrystals capable of

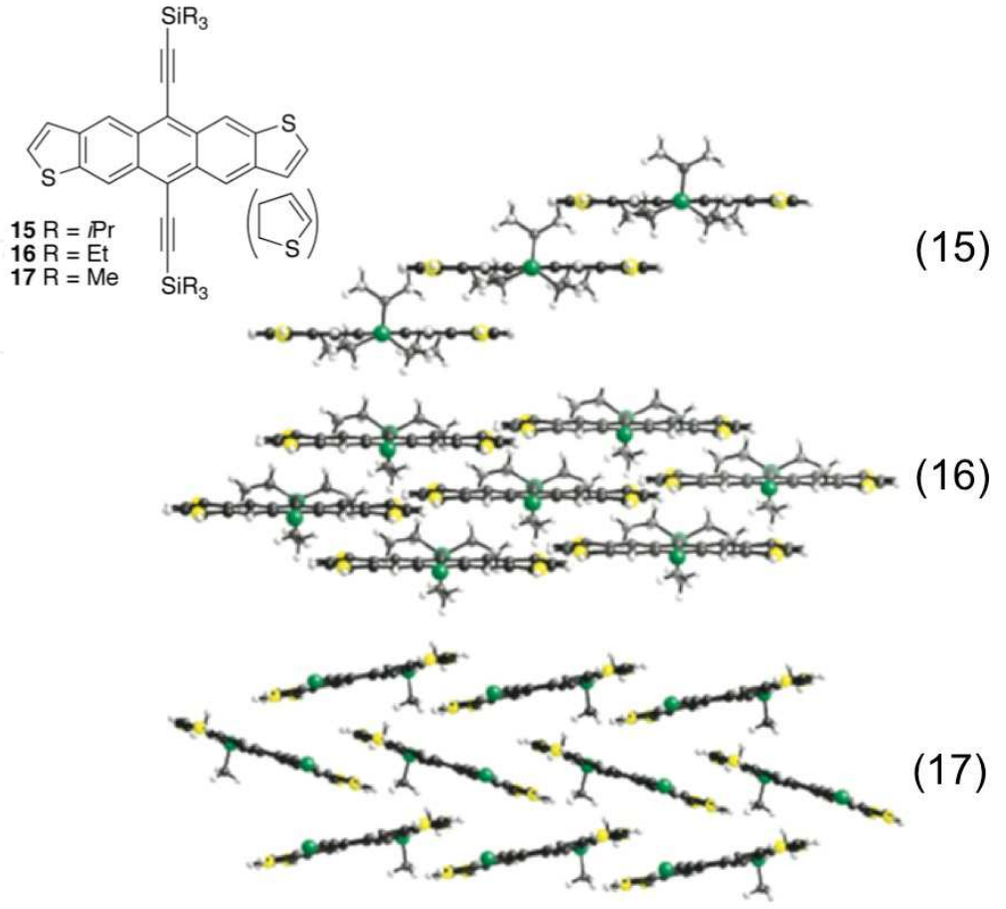


Figure 11. Crystal structure of anthradithiophenes **15 – 16** and their corresponding crystal structures. The alkyl groups on the front-most silicon atoms have been omitted for clarity. (Adapted with permission from reference 42c. Copyright 2005 American Chemical Society).

diffracting X-rays and giving diffraction patterns similar to bulk materials. This was achieved by inkjet printing a solution of the semiconductor in close proximity to a droplet of an antisolvent leading to slow crystallization as the solvents mix and evaporate. The crystals of a benzothiophene-based molecule obtained using this technique exhibit average mobilities of 16.4 $cm^2/V•s$ which are similar to that of rubrene single crystal devices.

The Bao group has actively been pursuing OFET technologies and has introduced patterned growth techniques that have the potential to grow crystals directly on devices obviating the need for manual manipulation of delicate crystals as is required in the vapor growth method.[44] Patterned growth is achieved by using a pre-patterned, self assembled monolayer as a growth template. Takeya and coworkers have introduced an oriented growth method[3, 45] where an inclined substrate and a "liquid-sustaining piece" allow high quality crystals to form on a SiO_2 coated substrate. The resulting materials were single crystalline as confirmed by X-ray diffraction and gave mobilities on the order of 2 – 6 $cm^2/V•s$. Thus, it can be seen that high quality single crystals with good mobility characteristics can be obtained by solution methods.

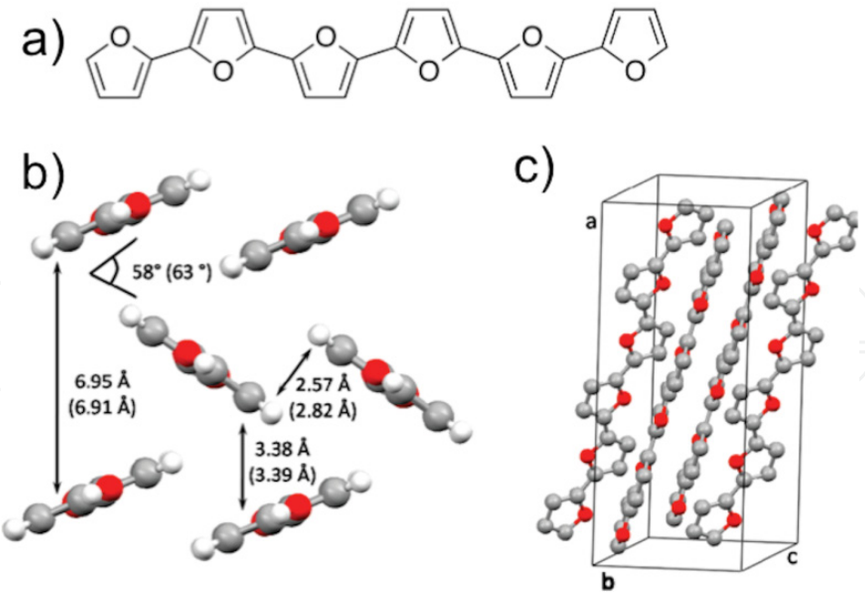


Figure 12. (a) The molecular structure of α-furan hexamer **10** and its crystal packing (b) and (c). The values given in parenthesis are for the thiophene analogue. (Adapted with permission from reference 46. Copyright 2010 American Chemical Society).

While significant effort has gone into new methods of growing high quality crystals and improving the solubility of acenes known to exhibit good performance in OFETs, effort is also directed toward the design of new materials with improved properties, such as smaller intramolecular distances in the solid state, that would lead to improved mobilities. While attention has been focused largely on thiophene based compounds[47] a recent report by Bendikov and coworkers[46] used X-ray crystallography, among other techniques, to reexamine the solid state structure of furan based materials. In particular, they synthesized and studied a series of furan oligomers including α-furan hexamer **10**, the structure and crystal packing of which is shown in Figure 12. When compared to the thiophene analogue,[48] **10** was found to exhibit closer packing (2.57 Å for **10** versus 2.89 Å for the thiophene analogue) and shorter inter-ring C-C bond distances indicating less aromatic character and more quinoidal character, both of which could facilitate better charge transport in furan-based materials. The Bendikov group has also explored OFETs from oligofuran materials,[49] and a recent study showed that solution grown crystals of a naphthodifuran gave mobilities of 3.6 $cm^2/V•s$ despite exhibiting herringbone packing, which leads to less than optimal intermolecular π-orbital overlap.[50] Thus, it appears that furan based crystalline semiconductors, with further optimization and crystal engineering, could eventually surpass their thiophene analogues.

Given the high mobilities intrinsic to single crystalline acene type semiconductors, it would seem that single crystalline materials would be well suited for OPVs, which similar to OFETs, require high mobility materials, but also require materials able to efficiently absorb solar energy. There are, however, few examples of single crystal organic photovoltaics[51] as most research is devoted to polymeric materials,[52] solution processable small molecule semiconductors,[53] and dye-sensitized solar cells.[54] Recently, Yang and coworkers assembled

a solar cell based on a single crystal of tetracene (shown in Figure 9) as the light absorbing layer and a C_{60} electron transport layer.[55] The device showed efficiencies that were less than 1%, and efficiency depended critically on the thickness of the crystal used in addition to the crystal face that was irradiated. The authors hypothesized that the device suffered from low performance because of the poor absorption of visible light by tetracene. Campione and coworkers similarly, examined single crystal photovoltaic devices based on rubrene, perylene, α-quarterthiophene, and tetracene without employing a C_{60} layer. While the voltage generated by the cell was adequate, the current generated was very low giving efficiencies that were on the order of 10^{-5}%. The authors attribute the low performance to a high rate of exciton recombination, which they say does not necessarily preclude the use of single crystals in solar cells, but may necessitate the use of electron accepting materials to ensure a higher propensity for exciton separation in the active layer. Higher efficiencies have been obtained using organic materials; Kippelen and coworkers achieved an efficiency of ~2.7 % using a cell consisting of pentacene and C_{60}, however, the active layer was polycrystalline.[56]

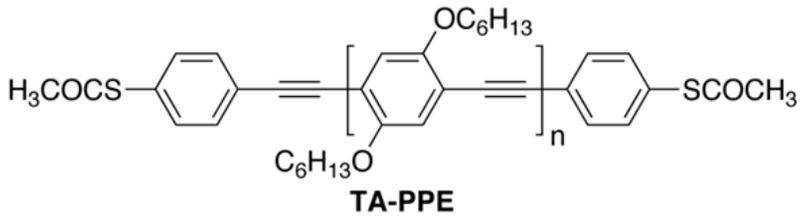


Figure 13. The molecular structure of **TA-PPE**.

Single crystal based devices show impressive mobilities, yet are not suitable for use when larger surface area coverage is desired such as in manufacturing displays and some solar cells, both of which are intensely pursued by academic and industrial groups seeking to commercialize these technologies. Polymeric and molecular materials amenable to spin coating and spray coating methods are ideally suited for coverage of large areas, but the mobilities resulting from amorphous and polycrystalline morphologies are orders of magnitude lower than those obtained for small single crystals. In an effort to close this gap, self-assembly processes have been examined for the generation of morphologies conducive to good charge transport and concomitant application in large area devices. In particular, nano-scale wires based on organic materials have been shown to be highly crystalline in nature, thus translating into effective charge transport materials[57] using simple and inexpensive solution methods.

Conjugated polymer nanowires with the potential for high mobility have been observed, although polymeric materials are typically spin coated or spray coated from dilute solutions giving amorphous films after solvent evaporation. In a prototypical example, however, careful and controlled deposition of the polymer **TA-PPE** (Figure 13) gave crystalline nanowires.[58] These nanowires were obtained by slow evaporation (over a period of days) of a tetrahydrofuran solution of polymer with concentrations ranging from 0.05 – 0.10 mg/mL. When incorporated into an OFET, the nanowires exhibited mobilities on the order of 0.01 –

0.1 $cm^2/V•s$, which were 3 – 4 orders of magnitude higher than the mobilities obtained from an amorphous film of **TA-PPE** obtained by spin coating. The slow evaporation ensured good ordering of the polymer wires as shown in Figure 14. Selected Area Electron Diffraction (SAED) gave sharp diffraction peaks indicating a high level of order as manifested in the high mobility values. Thus, conditions that allow polymer units to organize into higher order morphologies may be broadly applicable.

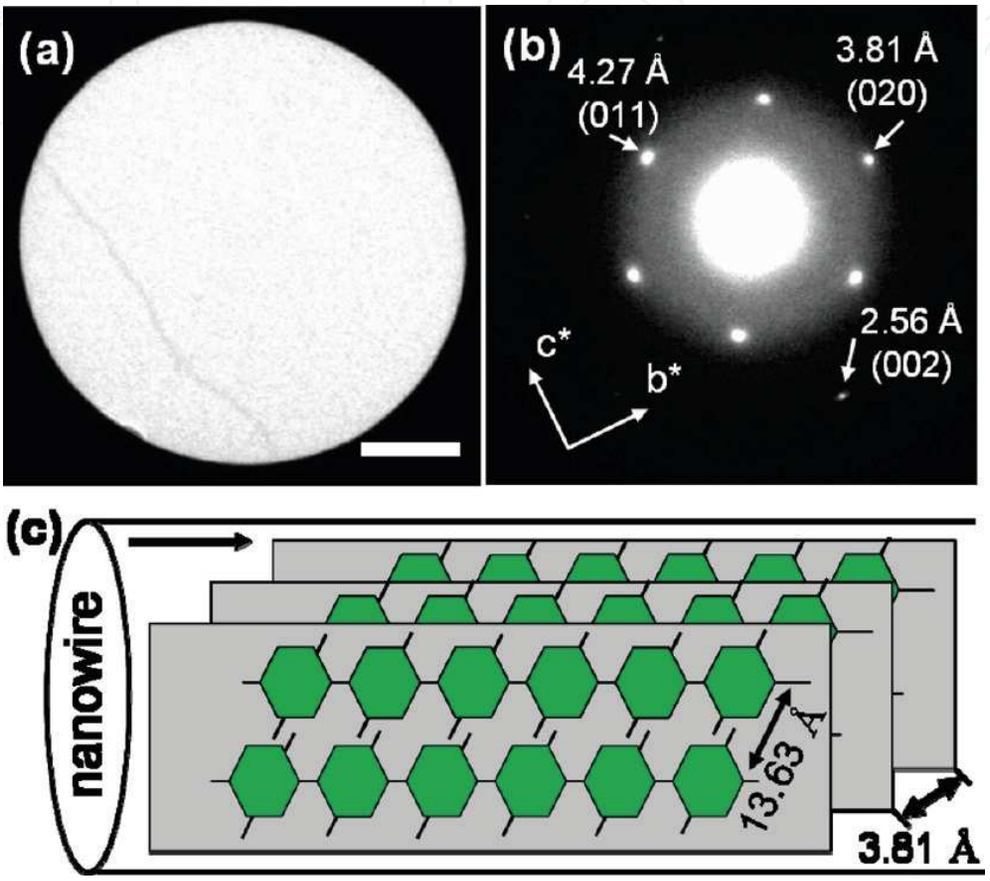


Figure 14. (a) TEM image of an individual TA-PPE nanowire (scale bar: 150 nm) and (b) its corresponding SAED pattern. (c) Schematic diagram of possible molecular packing in the one-dimensional nanowires; for clarity the end-capping groups have been omitted. (Adapted with permission from reference 58. Copyright 2009 American Chemical Society).

Molecular materials with a propensity to form ordered, π-stacks have also demonstrated the ability to form crystalline molecular wires. A dianthracene diester gave crystals that packed with good π-overlap between neighboring anthracene units.[59] Crystalline nanorods, when irradiated with UV light, underwent a [2+2] photopolymerzation reaction in a crystal-to-crystal type transformation. While the resulting polymer was not well suited to charge transport, the authors clearly demonstrated how single crystalline nanorods could be used to give other materials with application in organic electronics. In a similar study, a dicyanovinyl substituted anthracene molecule formed nanowires when films were cast from dichloromethane solution. These nanowires gave remarkably clear SAED patterns proving the single crystalline organization of the component molecules. Moreover, while the

mobility properties were not measured, the nanowires exhibit photoswitchable conductivity potentially allowing their use in photodetectors.

For most electronic applications, crystalline organic compounds still lag behind their inorganic counterparts in terms of device performance; however, the gap has been steadily decreasing. Given the continuous rapid advances of organic crystalline semiconductors, these materials may soon replace traditional inorganics and usher in an era of carbon-based electronic devices.

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4. References

[1] (a) Braga, A. F. B.; Moreira, S. P.; Zampieri, P. R.; Bacchin, J. M. G.; Mei, P. R., *Sol. Energy Mater. Sol. Cells* 2008, *92* (4), 418-424; (b) Mei, P. R.; Moreira, S. P.; Cardoso, E.; Cortes, A. D. S.; Marques, F. C., *Sol. Energy Mater. Sol. Cells* 2012, *98*, 233-239; (c) Taft, E. A.; Horn, F. H., *J. Electrochem. Soc.* 1958, *105* (2), 81-83.

[2] (a) Kloc, C.; Simpkins, P. G.; Siegrist, T.; Laudise, R. A., *J. Cryst. Growth* 1997, *182* (3-4), 416-427; (b) Laudise, R. A.; Kloc, C.; Simpkins, P. G.; Siegrist, T., *J. Cryst. Growth* 1998, *187* (3-4), 449-454.

[3] Uemura, T.; Hirose, Y.; Uno, M.; Takimiya, K.; Takeya, J., *Applied Physics Express* 2009, *2* (11), 111501.

[4] Dürr, H.; Bous-Laurent, H., *Photochromism: Molecules and Systems*. Elsevier: Amsterdam, 1990.

[5] Crano, J. C.; Guglielmetti, R. J., *Organic Photochromic and Thermochromic Compounds*. Plenum Press: New York, 1999.

[6] Dürr, H.; Bouas-Laurent, H., *Photochromism : molecules and systems*. Rev. ed.; Elsevier: Amsterdam ; Boston, 2003; p liii, 1044 p.

[7] (a) Evans, R. A.; Hanley, T. L.; Skidmore, M. A.; Davis, T. P.; Such, G. K.; Yee, L. H.; Ball, G. E.; Lewis, D. A., *Nat. Mater.* 2005, *4* (3), 249-253; (b) Evans, R. A.; Such, G. K., *Aust. J. Chem.* 2005, *58* (12), 825-830; (c) Such, G. K.; Evans, R. A.; Davis, T. P., *Macromolecules* 2004, *37* (26), 9664-9666; (d) Such, G. K.; Evans, R. A.; Davis, T. P., *Macromolecules* 2006, *39* (4), 1391-1396.

[8] Patel, D. G.; Paquette, M. M.; Kopelman, R. A.; Kaminsky, W.; Ferguson, M. J.; Frank, N. L., *J. Am. Chem. Soc.* 2010, *132* (36), 12568-12586.

[9] Hirshberg, Y., *J. Am. Chem. Soc.* 1956, *78* (10), 2304-2312.

[10] Chu, N. Y. C., *Can. J. Chem.* 1983, *61* (2), 300-305.

[11] Bénard, S.; Yu, P., *Chem. Commun.* 2000, (1), 65-66.

[12] Bénard, S.; Yu, P., *Adv. Mater.* 2000, *12* (1), 48-50.

[13] Patel, D. G.; Benedict, J. B.; Kopelman, R. A.; Frank, N. L., *Chem. Commun.* 2005, (17), 2208-2210.
[14] Harada, J.; Uekusa, H.; Ohashi, Y., *J. Am. Chem. Soc.* 1999, *121* (24), 5809-5810.
[15] Harada, J.; Kawazoe, Y.; Ogawa, K., *Chem. Commun.* 2010, *46* (15), 2593-2595.
[16] Kobatake, S.; Yamada, T.; Uchida, K.; Kato, N.; Irie, M., *J. Am. Chem. Soc.* 1999, *121* (11), 2380-2386.
[17] Yamada, T.; Kobatake, S.; Muto, K.; Irie, M., *J. Am. Chem. Soc.* 2000, *122* (8), 1589-1592.
[18] Irie, M.; Uchida, K., *Bull. Chem. Soc. Jpn.* 1998, *71* (5), 985-996.
[19] (a) Kobatake, S.; Hasegawa, H.; Miyamura, K., *Cryst. Growth. Des.* 2011, *11* (4), 1223-1229; (b) Kobatake, S.; Kuma, S.; Irie, M., *J. Phys. Org. Chem.* 2007, *20* (11), 960-967; (c) Liu, G.; Liu, M.; Pu, S.; Fan, C.; Cui, S., *Tetrahedron* 2012, *68* (10), 2267-2275; (d) Liu, G.; Pu, S.; Wang, X., *Tetrahedron* 2010, *66* (46), 8862-8871; (e) Matsuda, K.; Takayama, K.; Irie, M., *Inorg. Chem.* 2003, *43* (2), 482-489; (f) Ohara, H.; Morimoto, M.; Irie, M., *Photochem. Photobiol. Sci.* 2010, *9* (8), 1079-1081; (g) Pu, S.; Liu, G.; Shen, L.; Xu, J., *Org. Lett.* 2007, *9* (11), 2139-2142.
[20] Brayshaw, S. K.; Schiffers, S.; Stevenson, A. J.; Teat, S. J.; Warren, M. R.; Bennett, R. D.; Sazanovich, I. V.; Buckley, A. R.; Weinstein, J. A.; Raithby, P. R., *Chem. Eur. J.* 2011, *17* (16), 4385-4395.
[21] Colombier, I.; Spagnoli, S.; Corval, A.; Baldeck, P. L.; Giraud, M.; Léaustic, A.; Yu, P., *Mol. Cryst. Liq. Cryst.* 2005, *431* (1), 495-499.
[22] Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M., *Nature* 2007, *446* (7137), 778-781.
[23] Morimoto, M.; Irie, M., *J. Am. Chem. Soc.* 2010, *132* (40), 14172-14178.
[24] Koshima, H.; Ojima, N.; Uchimoto, H., *J. Am. Chem. Soc.* 2009, *131* (20), 6890-6891.
[25] Koshima, H.; Takechi, K.; Uchimoto, H.; Shiro, M.; Hashizume, D., *Chem. Commun.* 2011, *47* (41), 11423-11425.
[26] Matsuda, K.; Irie, M., *J. Am. Chem. Soc.* 2000, *122* (30), 7195-7201.
[27] (a) Boillot, M.-L.; Chantraine, S.; Zarembowitch, J.; Lallemand, J.-Y.; Prunet, J., *New J. Chem.* 1999, 179-183; (b) Boillot, M.-L.; Roux, C.; Audiere, J.-P.; Dausse, A.; Zarembowitch, J., *Inorg. Chem.* 1996, *35*, 3975-3980; (c) Roux, C.; Zarembowitch, J.; Gallois, B.; Granier, T.; Claude, R., *Inorg. Chem.* 1994, *33* (10), 2273.
[28] Takahashi, K.; Hasegawa, Y.; Sakamoto, R.; Nishikawa, M.; Kume, S.; Nishibori, E.; Nishihara, H., *Inorg. Chem.* 2012, *51* (9), 5188-5198.
[29] Mas-Torrent, M.; Rovira, C., *Chem. Rev.* 2011, *111* (8), 4833-4856.
[30] Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A., *Chem. Rev.* 2005, *105* (4), 1491-1546.
[31] (a) Anthony, J. E., *Chem. Rev.* 2006, *106* (12), 5028-5048; (b) Anthony, J. E., *Angew. Chem. Int. Ed.* 2008, *47* (3), 452-483; (c) Würthner, F.; Schmidt, R., *ChemPhysChem* 2006, *7* (4), 793-797.
[32] Jurchescu, O. D.; Baas, J.; Palstra, T. T. M., *Appl. Phys. Lett.* 2004, *84* (16), 3061-3063.
[33] Reese, C.; Bao, Z., *Mater. Today* 2007, *10* (3), 20-27.
[34] Hasegawa, T.; Takeya, J., *Science and Technology of Advanced Materials* 2009, *10* (2).
[35] Jurchescu, O. D.; Meetsma, A.; Palstra, T. T. M., *Acta Cryst. B* 2006, *62* (2), 330-334.

[36] Ding, H.; Reese, C.; Makinen, A. J.; Bao, Z.; Gao, Y., *Appl. Phys. Lett.* 2010, *96* (22), 3.
[37] Podzorov, V.; Pudalov, V. M.; Gershenson, M. E., *Appl. Phys. Lett.* 2003, *82* (11), 1739-1741.
[38] Podzorov, V.; Menard, E.; Borissov, A.; Kiryukhin, V.; Rogers, J. A.; Gershenson, M. E., *Phys. Rev. Lett.* 2004, *93* (8), 086602.
[39] da Silva Filho, D. A.; Kim, E. G.; Brédas, J. L., *Adv. Mater.* 2005, *17* (8), 1072-1076.
[40] Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A., *Science* 2004, *303* (5664), 1644-1646.
[41] Vehoff, T.; Baumeier, B.; Troisi, A.; Andrienko, D., *J. Am. Chem. Soc.* 2010, *132* (33), 11702-11708.
[42] (a) Anthony, J. E.; Eaton, D. L.; Parkin, S. R., *Org. Lett.* 2002, *4* (1), 15-18; (b) Payne, M. M.; Odom, S. A.; Parkin, S. R.; Anthony, J. E., *Org. Lett.* 2004, *6* (19), 3325-3328; (c) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N., *J. Am. Chem. Soc.* 2005, *127* (14), 4986-4987; (d) Purushothaman, B.; Bruzek, M.; Parkin, S. R.; Miller, A.-F.; Anthony, J. E., *Angew. Chem. Int. Ed.* 2011, *50* (31), 7013-7017.
[43] Minemawari, H.; Yamada, T.; Matsui, H.; Tsutsumi, J.; Haas, S.; Chiba, R.; Kumai, R.; Hasegawa, T., *Nature* 2011, *475* (7356), 364-367.
[44] (a) Briseno, A. L.; Aizenberg, J.; Han, Y.-J.; Penkala, R. A.; Moon, H.; Lovinger, A. J.; Kloc, C.; Bao, Z., *J. Am. Chem. Soc.* 2005, *127* (35), 12164-12165; (b) Briseno, A. L.; Mannsfeld, S. C. B.; Ling, M. M.; Liu, S.; Tseng, R. J.; Reese, C.; Roberts, M. E.; Yang, Y.; Wudl, F.; Bao, Z., *Nature* 2006, *444* (7121), 913-917.
[45] Soeda, J.; Hirose, Y.; Yamagishi, M.; Nakao, A.; Uemura, T.; Nakayama, K.; Uno, M.; Nakazawa, Y.; Takimiya, K.; Takeya, J., *Adv. Mater.* 2011, *23* (29), 3309-3314.
[46] Gidron, O.; Diskin-Posner, Y.; Bendikov, M., *J. Am. Chem. Soc.* 2010, *132* (7), 2148-2150.
[47] Perepichka, I. F.; Perepichka, D. F., *Handbook of thiophene-based materials*. Wiley: Hoboken, 2009.
[48] Horowitz, G.; Bachet, B.; Yassar, A.; Lang, P.; Demanze, F.; Fave, J. L.; Garnier, F., *Chem. Mater.* 1995, *7* (7), 1337-1341.
[49] Gidron, O.; Dadvand, A.; Sheynin, Y.; Bendikov, M.; Perepichka, D. F., *Chem. Commun.* 2011, *47* (7), 1976-1978.
[50] Mitsui, C.; Soeda, J.; Miwa, K.; Tsuji, H.; Takeya, J.; Nakamura, E., *J. Am. Chem. Soc.* 2012, *134* (12), 5448-5451.
[51] (a) Bredas, J.-L.; Durrant, J. R., *Acc. Chem. Res.* 2009, *42* (11), 1689-1690; (b) Clarke, T. M.; Durrant, J. R., *Chem. Rev.* 2010, *110* (11), 6736-6767.
[52] Günes, S.; Neugebauer, H.; Sariciftci, N. S., *Chem. Rev.* 2007, *107* (4), 1324-1338.
[53] (a) Dang, X.-D.; Tamayo, A. B.; Seo, J.; Hoven, C. V.; Walker, B.; Nguyen, T.-Q., *Adv. Funct. Mater.* 2010, *20* (19), 3314-3321; (b) Roncali, J., *Acc. Chem. Res.* 2009, *42* (11), 1719-1730; (c) Tamayo, A. B.; Tantiwiwat, M.; Walker, B.; Nguyen, T.-Q., *J. Phys. Chem. C* 2008, *112* (39), 15543-15552; (d) Walker, B.; Tamayo, A.; Duong, D. T.; Dang, X. D.; Kim, C.; Granstrom, J.; Nguyen, T. Q., *Advanced Energy Materials* 2011, *1* (2), 221-229.
[54] (a) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H., *Chem. Rev.* 2010, *110* (11), 6595-6663; (b) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.;

Liska, P.; Vlachopoulos, N.; Grätzel, M., *J. Am. Chem. Soc.* 1993, *115* (14), 6382-6390; (c) O'Regan, B.; Grätzel, M., *Nature* 1991, *353* (6346), 737-740.
[55] Tseng, R. J.; Chan, R.; Tung, V. C.; Yang, Y., *Adv. Mater.* 2008, *20* (3), 435-438.
[56] Yoo, S.; Domercq, B.; Kippelen, B., *Appl. Phys. Lett.* 2004, *85* (22), 5427-5429.
[57] Briseno, A. L.; Mannsfeld, S. C. B.; Jenekhe, S. A.; Bao, Z.; Xia, Y., *Mater. Today* 2008, *11* (4), 38-47.
[58] Dong, H.; Jiang, S.; Jiang, L.; Liu, Y.; Li, H.; Hu, W.; Wang, E.; Yan, S.; Wei, Z.; Xu, W.; Gong, X., *J. Am. Chem. Soc.* 2009, *131* (47), 17315-17320.
[59] Al-Kaysi, R. O.; Dillon, R. J.; Kaiser, J. M.; Mueller, L. J.; Guirado, G.; Bardeen, C. J., *Macromolecules* 2007, *40* (25), 9040-9044.